

BASF AG  
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231/00

Preparation of new or known 1-unsubstituted 4-benzoyl-pyrazole derivatives useful as pre- or post-emergence, total or selective herbicides, from 1-substituted analog and acid (Ger)

C2000-134336 (NAE AL AM AT AU AZ BA BB BG BR BY CA CH  
CN CR CU CZ DE DK DM EE ES FI GB GD GE GH  
GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK  
LR LS LT LU LV MA MD MG MK MN MW MX NO  
NZ PL PT RU RO SD SE SG SI SK SL TJ TM TR TT  
TZ UA UG US UZ VN YU ZA ZW) (RIAT BE CH CY  
DE DK EA ES FI FR GB GH GM GR IE IT KE LS LU  
MC MW NL OA PT SD SE SL SZ TZ UG ZW)

Addnl. Data: NEIDLEIN U, GOETZ N, MISSLITZ U, BAUMANN E,  
VON DEYN W, KUDIS S, LANGEMANN K, MAYER G,  
WITSCHER M, OTTEN M, WESTPHALEN K, WALTER  
H  
1999.12.01 1999-WO-EP09343

NOVELTY

(1-106, 14-11, 14-12B) .2

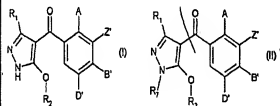
Preparation of 1-unsubstituted 4-benzoyl-5-oxy-pyrazoles (I) involves treating a 1-(branched alkyl, alkenyl or alkynyl or benzyl)-substituted analog (II) with acid to cause elimination of an olefin or alcohol.

#### DETAILED DESCRIPTION

Preparation of 1-unsubstituted 4-benzoyl-pyrazoles of formula (I) involves treating a 1-substituted analog of formula (II) with an inorganic or organic acid at pH less than 2, to cause elimination of an olefin or alcohol.

reactant (V)

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$R_1 = H \text{ or } T^*$ ;  
 $R_2 = H, \text{ alkyl, alkenyl, alkynyl, benzyl, benzoyl, } C(O)OT^*, -T^*,$   
 $C(O)OH, -T^*, -C(O)OT^*, SO_2T^* \text{ or } SO_2\text{-phenyl (all optionally}$   
 $\text{substituted (as by } T^*, OT^*, ST^*, \text{ halogen, OH, NH}_2, NO_2 \text{ or}$   
 $CN);$   
 $T^* = 1-4C \text{ alkyl};$   
 $T^* = T \text{ or } 1-4C \text{ haloalkyl};$   
 $A, B', D' = \text{alkyl, alkenyl, alkyl or } OT^* \text{ (all os by halogen, OH, } OT^*$   
 $\text{or CN) or } H, \text{ halogen, OH, CN, NO}_2, -(Y)_n-S(O)_mR_3 \text{ or}$   
 $-(Y)_n-C(O)R_4;$   
 $Z^* = \text{as for A, phenyl (os by } T^*, \text{ halogen, OH, CN or NO}_2) \text{ or a 5- or 6-}$   
 $\text{membered saturated or unsaturated heterocycle containing 1-3}$   
 $\text{of O, S and N (os by halogen, CN, NO}_2, -C(O)R_4, T^*, 3-8C$

cycloalkyl,  $OT^*, ST^*, N(T^*)_2$ , phenyl (itself os by halogen, CN,  $NO_2$  or  $T^*$ ) or oxo (optionally as the hydroxy tautomer) and optionally fused with a phenyl ring (os by halogen, CN,  $NO_2$  or  $T^*$ ), a carbocycle or a second heterocycle (os by halogen, CN,  $NO_2, T^*, N(T^*)_2$  or  $OT^*$ ) to form a bicyclic system);

$Y^* = O \text{ or } NR_5$ ;

$n = 0 \text{ or } 1$ ;

$m = 0-2$ ;

$R_3 = T^* \text{ or } NR_5R_6$ ;

$R_4 = OH, T^*, OT^* \text{ or } NR_5R_6$ ;

$R_5 = H \text{ or } T^*$ ;

$R_6 = T^*$ ;

$R_7 = \text{branched 3-12C alkyl, 3-12C alkenyl or 4-12C alkynyl (os by}$   
 $\text{halogen or } OT^*) \text{ or benzyl (os by halogen, CN, NO}_2, 1-4C$   
 $\text{haloalkyl, } SO_2T^* \text{ or } C(O)T^*);$

An INDEPENDENT CLAIM is included for (I) and their salts as new compounds, provided that  $Z^*$  is other than 5-isoxazolyl or 5-pyrazolyl.

#### ACTIVITY

Herbicidal, 4-(3-(4,5-Dihydro-isoxazol-3-yl)-4-methanesulfonyl-2-methylbenzoyl)-5-(2,4-difluorobenzoyloxy)-1H-pyrazole (Ia) at 0.125

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kg/ha post-emergence showed excellent herbicidal activity (no quantitative results given) against weeds such as *Chenopodium album*, *Echinochloa crus-galli* and *Setaria viridis*.

#### MECHANISM OF ACTION

None given.

#### USE

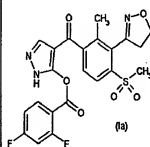
(I) are herbicides (claimed for the new compounds (I)). They are useful as total herbicides or (at lower application rates) selective herbicides for controlling grasses and other weeds in crops such as wheat, rice, maize, soya and cotton.

#### ADVANTAGE

The process gives (I) in high yield.

#### SPECIFIC COMPOUNDS

9 Compounds (I) are disclosed, e.g. 4-(3-(4,5-dihydro-isoxazol-3-yl)-4-methanesulfonyl-2-methylbenzoyl)-5-(2,4-difluorobenzoyloxy)-1H-pyrazole of formula (Ia).



#### ADMINISTRATION

Application rate is 0.001 - 3 (preferably 0.01 - 1) kg/ha, pre- or post-emergence.

#### EXAMPLE

A solution of 3-(4,5-dihydro-isoxazol-3-yl)-4-methanesulfonyl-2-

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(con't)

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methylbenzoyl chloride (1.0 g) in dioxan was treated with N-tert-butyl-pyrzalone (0.61 g) and dicyclohexyl carbodiimide (0.79 g), stirred overnight at room temperature, filtered, treated with potassium carbonate (0.58 g), heated at reflux for 3 hours and evaporated. The residue was worked up to give 2-tert-butyl-2H-pyrazol-3-yl 3-(4,5-dihydro-isoxazol-3-yl)-4-methanesulfonyl-2-methylbenzoate (0.81 g; 57 %). A solution of the above product (0.5 g) in acetonitrile (10 ml) was treated with trifluoromethanesulfonic acid (0.37 g), heated at reflux for 5 hours and evaporated. The residue was worked up to give 4-(3-(4,5-dihydro-isoxazol-3-yl)-4-methanesulfonyl-2-methylbenzoyl)-5-hydroxy-1H-pyrazole (0.27 g; 54 %).

#### DEFINITIONS

Preferred Definitions:

Unless specified otherwise alkyl groups are 1-6C and alkenyl or alkynyl groups are 2-6C.

In the new compounds:

Z' = oxazolyl, 3- or 4-isoxazolyl, thiazolyl, isothiazolyl, 3- or 4-pyrazolyl, imidazolyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, pyrrolinyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, pyrazolyl, imidazolyl or dioxolanyl;

R<sub>1</sub>, R<sub>2</sub> = H or T<sup>+</sup>;

A, B', D' = H, T, OT<sup>+</sup>, ST<sup>+</sup>, SO<sub>2</sub>T<sup>+</sup>, halogen, OH, CN or NO<sub>2</sub>.

In the process:

R<sub>3</sub> = α-branched 3-6C alkyl or benzyl (as in the 4-position by Cl, CN, NO<sub>2</sub>, CF<sub>3</sub>, SO<sub>2</sub>CH<sub>3</sub> or acyl).

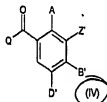
#### TECHNOLOGY FOCUS

Organic Chemistry - Preferred Process: The organic acid is trifluoromethanesulfonic or trichloroacetic acid; and the inorganic acid is sulfuric, nitric, hydrochloric or hydrobromic acid. Reaction is carried out in a solvent, specifically acetonitrile, dimethyl formamide, dioxan, tetrahydrofuran, toluene or chlorobenzene.

(II) are prepared by acylating hydroxy-pyrazoles of formula (III) with benzoyl halides of formula (IV), followed by catalytic rearrangement of the acylation product.

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Q = halogen.

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